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Description

This invention relates to a multi-layered vessel whose sectional structure of synthetic resin has at least a triple-layer used as a vessel for containing carbonated beverages or fruit juice.

Blow or orientation blow molded plastic packing vessels are light in weight and have a falling strength but are inferior in heat resistance and gas barrier properties to glass. In the case where these vessels are used as vessels for beverages which refrain from permeation of fruit juice, oxygen, carbonic acid or the like which require to be filled at high temperature, a further improvement has been necessitated.

In view of the foregoing, a multi-layered vessel of at least a triple-layer has been developed in which within the resin (for example, polyethyleneterephthalate) to be used to form a vessel body is provided, as an intermediate layer, other resin which makes up for the disadvantage of the first-mentioned resin. As other intermediate layers, an ethylene vinyl alcohol copolymer having excellent gas barrier properties, polycarbonate polyamide having a heat resistance and the like are used.

This vessel having a multi-layered construction can be produced by blow molding or orientation blow molding an extruded or injection molded multi-layered parison in a manner similar to the case of a single-layer construction, and an intermediate layer formed therein is positioned in the midst or internally of the resin which forms a vessel body. In the vessel body in which the intermediate layer is positioned in the midst of the resin, there is present no difference in wall thickness between two layers, an inner layer and an outer layer, defined by the intermediate layer, but where the intermediate layer is positioned one-sided inwardly, there is present a difference in wall thickness between the inner and outer layers, in which case the inner layer is materially thin as compared with that of the outer layer.

The distribution of the wall thickness of layers in the multi-layered vessel is decided by the distribution of the all thickness of a multi-layered bottomed parison extruded or injection molded, and a proportion of the wall thickness of the parison will be a proportion of the wall thickness of a vessel without modification.

Molding of a multi-layered bottom parison is effected by using a double nozzle composed of an outer flowpassage in communication with a nozzle orifice and an inner flowpassage opened in an extreme end of the outer flowpassage, as disclosed in U.S. Patent No. 4,174,413, and a first resin forming a parison body and a second resin forming an intermediate layer are injected into a cavity through the outer flowpassage and inner flowpassage, respectively.

The resins such as ethylene vinyl alcohol copolymer (EVOH), polyamide (FA) and the like increase in the quantity of permeation of oxygen, carbonic acid or the like as the moisture absorption increases. On the other hand, the biaxially oriented polyester resin used as bottles for carbonated beverages is lower in water vapor permeability than the aforementioned resin but the water vapor permeability is affected by the thickness as can be said generally in resins.

Therefore, in a multi-layered vessel in which an inner layer is formed in a small wall thickness, even if the resin forming a vessel is biaxially oriented polyethyleneterephtalate the gas barrier properties caused by the intermediate layer is materially decreased by the influence of the moisture absorption from the content, and the permeability of oxygen and carbonic acid increases. Therefore, such vessels are not suitable for use with beer, carbonated beverages and the like which are required to be stored for a long period of time, and in order to use such vessels as ones for food and drinks which refrain from permeation of oxygen, even a multi-layered vessels have to further increase its gas barrier properties.

EP-A-76 366 discloses a process for producing a three-layer tubular body comprising an inner layer, an outer layer and a barrier layer interposed there between proximate the outer surface, by use of a triple nozzle providing an annular slot for injecting the barrier material, said slot being interposed between two other annular slots through which are injected the materials of the two other layers, respectively.

3. OBJECT OF THE INVENTION

An object of the present invention is to provide a new molding method which comprises injection molding a multi-layered parison, which is capable of molding a multi-layered vessel wherein an inner layer is formed to have a greater thickness than an outer layer by an intermediate layer, by use of a double nozzle, and obtaining a multi-layered vessel having an excellent gas barrier properties or heat resistance from said multi -layered parison.

Accordingly, the present invention provides a method as defined in claim 1. for producing a vessel which comprises a first resin forming a body and a second resin which has greater gas barrier properties or heat resistance than that of the first resin and which is present as an intermediate layer of the body within the first resin, said body being provided with at least three layers, i.e., said intermediate layer, an inner layer and an outer layer which are defined by said intermediate layer, said inner layer being formed to be

materially greater in wall thickness than that of the outer layer by the provision of the intermediate layer formed one-sided toward the outer layer, and said intermediate layer being smaller in wall thickness than said outer layer.

4. BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partly enlarged fragmentary sectional view of a multi-layered vessel molded from a multi-layered parison molded according to the present invention.

FIG. 2 is a sectional view of a multi-layered parison molded according to the present invention.

FIGS. 3 to 5 are respectively sectional views of a nozzle portion and a mold showing the molding method of the present invention in order:

FIG. 3 is a view showing a state wherein a first resin forming a body of a multi-layered parison is partly injected;

FIG. 4A is a sectional view of a nozzle tip portion and a gate portion showing a state wherein a second resin forming an intermediate layer is injected into the resin forming the body;

FIG. 4B is a sectional view of a nozzle tip portion and a gate portion showing a state wherein the second resin is injected;

FIG. 4C is a sectional view of a nozzle tip portion and a gate portion showing a state wherein the first resin and second resin are simultaneously injected; and

FIG. 5 is a view showing a state wherein molding of a multi-layered parison has been completed.

FIG. 1 shows a multi-layered vessel 1 in the form of a bottle whose entirety has a triple-layered construction, in which an inner layer 11 and an outer layer 12 are formed from the same thermoplastic resin, and an intermediate layer 13 is formed from a thermoplastic resin having excellent gas barrier properties.

The intermediate layer 13 is provided one-sided toward the outer layer 12 whereby a wall thickness of the inner layer 11 is materially greater than that of the outer layer 12.

The ratio of wall thickness between the inner layer 11 and the outer layer 12 is preferably above 1 : 1.50, and the greater the wall thickness of the inner layer, the gas barrier properties are enhanced.

The aforesaid multi-layered vessel 1 can be produced blow or orientation blow molding a multi-layered parison 2 having a triple-layered construction in which a resin forming a parison body is defined into an inner layer 21 and an outer layer 22 which are different in wall thickness from each other by an intermediate layer 23 formed from the other resin into the first-mentioned resin.

This multi-layered parison 2 is injection molded by use of a double nozzle shown in FIG. 3 and others, that is, a double nozzle 3 coaxially provided with an outer flowpassage 32 in communication with a nozzle orifice 31 and an inner flowpassage 33 opened into the extreme end of the outer flowpassage 32.

In molding a multi-layered parison by use of a conventional double nozzle, a first resin forming a parison is injected from the outer flowpassage 32 into a mold 4 but in the present invention, a first resin 5 is injected from the inner flowpassage 33 and a resin 6 forming an intermediate layer is injected from the outer flowpassage 32. It is preferable that injection pressure of the resin 6 should be within such an extent that allows the first resin 5 to remain in the nozzle orifice 31 as a core.

Injection of the resin into the mold 4 is begun by injecting a suitable quantity of first resin 5 from the inner flowpassage 33. In this case, injection pressure is approximately 65 kg/cm^2 in case of polyethyleneterephtalate (hereinafter referred to as "PET"), and injection is carried out for about 3.5 sec., after which the injection is once stopped, and a second resin 6 is injected from the outer flowpassage 32 under the injection pressure of 90 kg/cm^2 for 0.1 to 1.0 sec.

The second resin 6, which is injected with the injection of the first resin 5 stopped, is to be one-sided externally of a cavity filled with the first resin 5, as shown in FIG. 4A.

This results from the fact that as shown in FIG. 4B, a part of the previously injected first resin 5 forms skin layers 5a and 5b by cooling caused by the mold 4, and the other part thereof remains in the form of a core 5c in the nozzle orifice 31 from the inner flowpassage 33, the core 5c causing the resin to prevent it from entry into the central portion of the first resin 5 from the center of the nozzle orifice 31 and to pass through the nozzle orifice 31 in a manner so as to spread open the periphery of the core 5c.

After the lapse of injection time, injection of the first resin 5 is again carried out with the injection of the second resin 6 kept to proceed. The injection time of the second resin 6 is about 1.6 sec. and the injection time of the first resin 5 after re-injection is about 3.4 sec., and the two resins forwardly flow between the skin layers 5a and 5b of the first resin 5 by cooling as shown in FIG. 4C. Thereby the outer skin layer 5b is moved away from the flowing first resin 5 by the second resin 5 and is formed into the outer layer 22 without increasing its thickness. The inner skin layer 5a is molten together with the first ressin 5 injected

along with the second resin 6 to increase a thickness thereof, where the thick inner layer 21 is formed. As the result, finally, as shown in FIG. 5, a multi-layered parison 2 having a triple-layered construction in which the intermediate layer 23 is positioned one-sided toward the outer layer 22 is formed.

The aforementioned step of injection molding uses an ethylene vinyl alcohol copolymer as the second resin 6. In case where the intermediate layer 23 is formed from polyamide which contains a methoxylene group, the second resin 6 is injected alone after the parison forming resin 5, after which the first resin 5 can be further injected alone or the second resin 6 can be inejcted while injecting the first resin 5.

However, whatever the injection timing of the second resin 2 may be, as far as the first resin 5 is first injected from the inner flowpassage 33 and the second resin 6 is then injected from the outer flowpassage 32, it is possible to mold the multi-layered parison 2 in which the inner layer 21 is partitioned to have a materially greater wall thickness than that of the outer layer 22 by the intermediate layer 23 formed from the second resin 6.

When the amount of injetion of the second resin 6 decreases, the wall thickness of the intermediate layer 23 also naturally descreases but there is no significant change in the wall thickness of the outer layer 22 and the wall thickness of the inner layer 21 increases.

Accordingly, the wall thicknesses of the inner layer 21 and the intermediate layer 22 can be adjusted from each other to enhance the gas barrier and heat resistant properties. As the case may be, the quantity of use of the second resin 6 which is generally considered to be expensive as compared with the first resin 5 can be reduced to lower the cost.

Next, gas barrier effects of a biaxially oriented triple-layered vessel produced by orientation blow molding the above-described multi-layered bottomed parison 2 in a conventional manner are given below:

<u>Embodiment and Comparative Example</u>

Kind of vessel:	Bottle with a round bottom for carbonated beverage, 0.7 lit., 26 g
First resin:	PET: TEIJIN TR-8550
Second resin:	PA: MXD-6 nylon
Second resin:	EVOH: KURARE EVERL E-105
Machine used:	ASB-50HT 107 (manufatured by NISSEI ASB)
Injection capacity:	First resin side: 3.50 oz (Ø38 screw) Second resin side: 1.0 oz (Ø19 screw)
Coefficient of permeation for oxygen and carbonic gas (per bottle):	cc/2 kg, 24 horus, 1 atmosphere
Oxygen permeation measuring unit:	MOCON, two-through gas permeation measuring unit
Carbonic gas permeation measuring unit:	MOCON, five-through gas permeation measuring unit (a 4-volume calcareous water filled vessel is measured)
Measuring conditions:	Relative humidity: inside - 100%RH, outside: 65% RH, Room temp. 24°C, one week remains left

Embodiments 1, 2 and Comparative Example 1

Structure of vessel: Outer layer/intermediate layer/inner layer

PET/PA/PET

Wall thickness of a shell of vessel (μ)	Emb. 1	Emb. 2	Comp.Exa. 1
Outer layer	80	59	182
Intermediate layer	38	39	41
Inner layer	143	170	53
Whole body	261	268	276
Ratio of outer layer/inner layer:	1/1.8	1/2.9	3.4/1
Coefficient of oxygen permeation	0.110	0.092	0.136
Coefficient of carbonic acid permeation	-	-	-

Embodiments 3, 4 and Comparative Example 2

Structure of vessel: Outer layer/intermediate layer/inner layer

PET/EVOH/PET

Wall thickness of a shell of vessel (μ)	Emb. 3	Emb. 4	Comp.Exa. 2
Outer layer	76	60	188
Intermediate layer	15	16	16
Inner layer	174	194	52
Whole body	265	270	261
Ratio of outer layer/inner layer	1/2.3	1/3.2	3.6/1
Coefficient of oxygen permeation	0.111	0.099	0.207
Coefficient of carbonic acid permeation	0.447	0.398	0.803

As will be evident from the above-described Embodiments and Comparative Examples, the gas barrier effect according to the present invention in which the inner layer is formed to have a greater thickness than that of the outer layer has been enhanced much more than that of the conventional construction in which the outer layer has a greater thickness.

Moreover, it is to be noted that if a heat resisting multi-layered vessel uses, as an intermediate layer, the heat resistant resin such as polycarbonate, polyacrylate polyethyleneterephtalate (U-POLYMER) or the like, the vessel having the inner layer greater in wall thickness is excellent in heat resistance, which induces no thermal deformation even at a temperature up to 85 °C.

Claims

1. A method for molding a multi-layered vessel, comprising :

providing a parison molding cavity for molding therein a multi-layered parison having a peripheral wall including at least an inner wall layer, an outer wall layer and an intermediate wall layer disposed between the inner and outel wall layers ;

coupling to said cavity a double nozzle injector having an outerflow passage which communicates into a nozzle orifice and having an inner flow passage opened in an extreme end of the outer flow passage ;

injecting through said inner flow passage a first resin for forming the inner and outer wall layers of the parison, and subsequently

injecting through the said outer flow passage a second resin having substantially improved gas barrier or heat resisting characteristics as compared to the first resin for forming the intermediate wall layer, the second resin being flowed substantially around the first resin remaining in the nozzle orifice so as to allow the second resin to surround the first resin in the parison molding cavity in a manner that

separates the first resin in the parison molding cavity into the inner and outer wall layers and further such that the thickness of the inner wall layer of the parison is substantially greater than that of the outer wall layer, and blow or orientation blow molding said multi-layered parison to mold a multi-layered vessel in which the inner layer is materially greater in wall thickness than that of the outer layer.

2. A method for molding a multi-layered vessel according to claim 1, including injecting first a predetermined quantity of the first resin from the inner flow passage into the parison molding cavity ;
   stopping injection of the first resin ;
   starting injection of the second resin from the outer flow passage in a manner that allows the second resin to surround substantially the first resin in the parison molding cavity ;
   restarting injection of the first resin after the lapse of a first predetermined time to obtain simultaneous injection of the first and second resins, and
   stopping injection of the second resin ; and
   stopping injection of the first resin after the lapse of a second predetermined time after stoppage of the injection of the second resin.

3. A method for molding a multi-layered vessel according to claim 1, wherein the second resin is injected with a predetermined pressure and at such time after the starting of the injection of the first resin such as to cause the wall thickness ratio of the inner wall layer to the outer wall layer to be greater than about 2.3 : 1.

4. A method for molding a multi-layered vessel according to claim 3, wherein the first resin is injected into the parison molding cavity at a pressure of approximately 65 kg/cm^2.

5. A method for molding a multi-layered vessel according to claim 4, wherein the second resin is injected at an injection pressure of about 90 kg/cm^2.

6. A method for molding a multi-layered vessel as in claim 2, wherein the first resin is initially injected for a period of about 3.5 seconds and the second resin is thereafter injected alone for a period of about 0.1 to 1.0 seconds.

7. A method for molding a multi-layered vessel as in claim 6, wherein, after restarting of the injection of the first resin, the first resin and second resin are injected together for a period of about 1.6 seconds.

Patentansprüche

1. Verfahren zum Formen eines mehrschichtigen Behälters, umfassend:
   Bereitstellen eines Vorformhohlraumes zum Formen eines mehrschichtigen Vorformlings mit einer Umfangswand, die mindestens eine Innenwandschicht, eine Außenwandschicht und eine Zwischenwandschicht Zwischen der Innen- und der Außenwandschicht aufweist;
   Ankuppeln eines Doppeldusen-Injektors mit einem Außenstromkanal, welcher mit einer Düsenöffnung kommuniziert, und einem Innenstromkanal, welcher in das äußerste Ende des Außenstromkanales mündet, an den Vorformhohlraum;
   Einspritzen eines ersten Harzes zum Formen der Innen-und der Außenwandschichten des Vorformlinges durch den Innenstromkanal und anschließend
   Einspritzen durch den Außenstromkanal eines zweiten Harzes mit einer wesentlich verbesserten Gasundurchlässigkeit oder Hitzebeständigkeit im Vergleich zum ersten Harz zum Formen der Zwischenwandschicht, wobei das zweite Harz im wesentlichen um das erste, in der Düsenmündung verbleibende Harz strömt, so daß das zweite Harz das erste Harz in dem Vorformhohlraum derart umgibt, daß das erste Harz im Vorformhohlraum in die Innen- und die Außenwandschicht aufgespalten wird, und ferner derart, daß die Wandstärke der Innenwandschicht des Vorformlings im wesentlichen größer als diejenige der Außenwandschicht gemacht wird, und Blasformen oder Orientierungsblasformen des mehrschichtigen Vorformlings zum Formen eines mehrschichtigen Behälters, bei den die Innenwandschicht eine deutlich größere Wandstärke als die Außenwandschicht aufweist.

2. Verfahren zum Formen eines mehrschichtigen Behälters nach Anspruch 1, umfassend das Einspritzen einer ersten vorbestimmten Menge des ersten Harzes aus dem Innenstromkanal in den Vorformhohlraum;

Stoppen der Einspritzung des ersten Harzes,
Starten der Einspritzung des zweiten Harzes über den Außenstromkanal in einer Weise, welche dem zweiten Harz im wesentlichen das Umgeben des ersten Harzes in dem Vorformhohlraum gestattet;
Erneutes Starten des Einspritzens des ersten Harzes nach Verstreichen einer ersten vorbestimmten Zeit zum Erzielen gleichzeitigen Einspritzens des ersten und des zweiten Harzes und
Stoppen des Einspritzens des zweiten Harzes und
Stoppen des Einspritzens des ersten Harzes nach Verstreichen einer zweiten vorbestimmten Zeit nach dem Stoppen des Einspritzens des zweiten Harzes.

3. Verfahren zum Formen eines mehrschichtigen Behälters nach Anspruch 1, bei dem das zweite Harz unter einem vorbestimmten Druck und zu einem solchen Zeitpunkt nach dem Starten des Einspritzens des ersten Harzes eingespritzt wird, daß das Wandstärkeverhältnis der Innenwandschicht zur Außenwandschicht größer als etwa 2,3 : 1 wird.

4. Verfahren zum Formen eines mehrschichtigen Gefässes nach Anspruch 3, bei dem das erste Harz in den Vorformhohlraum unter einem Druck von etwa 65 kg/cm^2 eingespritzt wird.

5. Verfahren zum Formen eines mehrschichtigen Gefässes nach Anspruch 4, bei dem das zweite Harz unter einem Einspritzdruck von etwa 90 kg/cm^2 eingespritzt wird.

6. Verfahren zum Formen eines mehrschichtigen Behälters nach Anspruch 2, bei dem das erste Harz anfänglich über eine Zeitdauer von etwa 3,5 Sekunden und anschließend das zweite Harz allein über eine Zeitdauer von etwa 0,1 bis 1,0 Sekunden eingespritzt werden.

7. Verfahren zum Formen eines mehrschichtigen Behälters nach Anspruch 6, bei dem nach Wiederaufnahme des Einspritzens des ersten Harzes dieses und das zweite Harz gemeinsam über eine Zeitdauer von etwa 1,6 Sekunden eingespritzt werden.

Revendications

1. Procédé de moulage d'un récipient à plusieurs couches, comprenant les étapes qui consistent à :
se munir d'une cavité de moulage d'une paraison pour y mouler une paraison à plusieurs couches possédant une paroi périphérique renfermant au moins une couche de paroi interne, une couche de paroi externe et une couche de paroi intermédiaire disposée entre la couche de paroi interne et la couche de paroi externe;
coupler à ladite cavité un injecteur à deux tuyères possédant un passage d'écoulement externe qui communique avec l'orifice d'une tuyère et possédant un passage d'écoulement interne qui s'ouvre à une extrémité du passage d'écoulement externe;
injecter dans ledit passage d'écoulement interne une première résine pour former la couche de paroi interne et la couche de paroi externe de la paraison, et ensuite
injecter dans ledit passage d'écoulement externe une seconde résine ayant des caractéristiques de barrière aux gaz ou de résistance à la chaleur sensiblement améliorées par rapport à la première résine pour former la couche de paroi intermédiaire, la seconde résine s'écoulant sensiblement autour de la première résine demeurant dans l'orifice de la tuyère, de manière à permettre à la seconde résine d'entourer la première résine dans la cavité de moulage de la paraison, de manière à séparer la première résine dans la cavité de moulage de la paraison en la couche de paroi interne et la couche de paroi externe, et aussi de manière à ce que l'épaisseur de la couche de paroi interne de la paraison soit sensiblement plus grande que celle de la couche de paroi externe, et mouler par soufflage ou par soufflage orienté ladite paraison à plusieurs couches, pour mouler un récipient à plusieurs couches dans lequel la couche interne a une épaisseur de paroi matériellement plus grande que la couche externe.

2. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 1, comprenant les étapes qui consistent à injecter d'abord une quantité prédéterminée de la première résine depuis le passage d'écoulement interne dans la cavité de moulage de la paraison;
arrêter l'injection de la première résine;
commencer l'injection de la seconde résine depuis le passage d'écoulement externe, de manière à permettre à la seconde résine d'entourer sensiblement la première résine dans la cavité de moulage de

la paraison;

redémarrer l'injection de la première résine après un premier laps de temps prédéterminé, pour obtenir l'injection simultanée de la première résine et de la seconde résine, et

arrêter l'injection de la seconde résine; et

arrêter l'injection de la première résine après un second laps de temps prédéterminé après l'injection de la seconde résine.

3. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 1, dans lequel la seconde résine est injectée sous une pression prédéterminée et à un moment, après le début de l'injection de la première résine, tel que le rapport entre les épaisseurs de paroi de la couche de paroi interne et de la couche de paroi externe soit supérieur à environ 2,3 : 1.

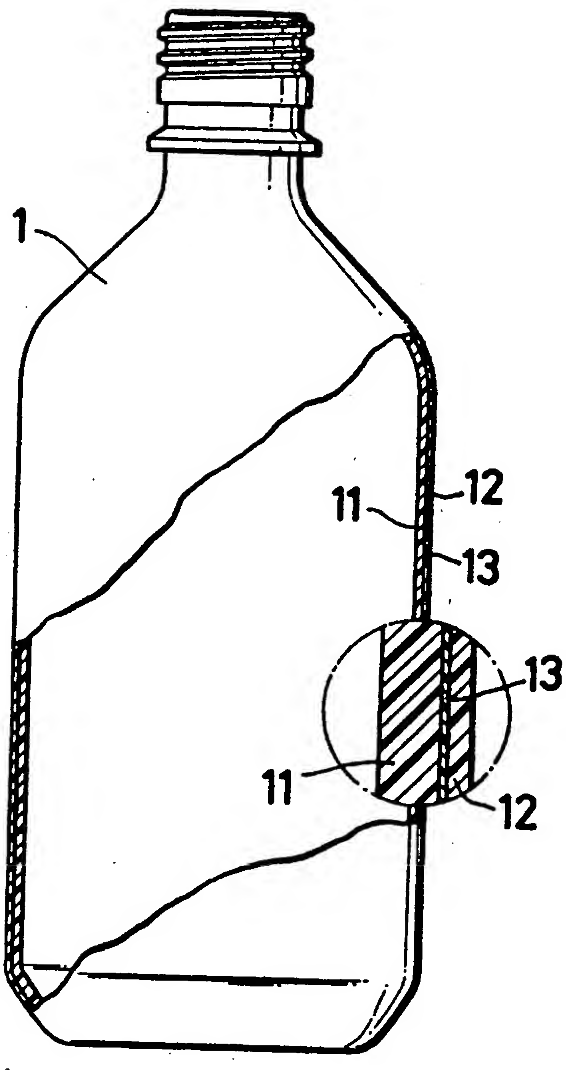
4. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 3, dans lequel la première résine est injectée dans la cavité de moulage de la paraison sous une pression d'environ 65 kg/cm^2.

5. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 4, dans lequel la seconde résine est injectée sous une pression d'injection d'environ 90 kg/cm^2.

6. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 2, dans lequel la première résine est initialement injectée pendant une durée d'environ 3,5 secondes et la seconde résine est injectée ensuite seule pendant une durée d'environ 0,1 à 1,0 secondes.

7. Procédé de moulage d'un récipient à plusieurs couches selon la revendication 6, dans lequel, après le redémarrage de l'injection de la première résine, la première résine et la seconde résine sont injectées ensemble pendant une durée d'environ 1,6 secondes.

F I G.1



F I G.2

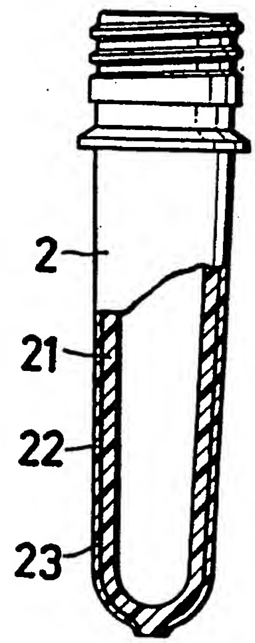


FIG.3

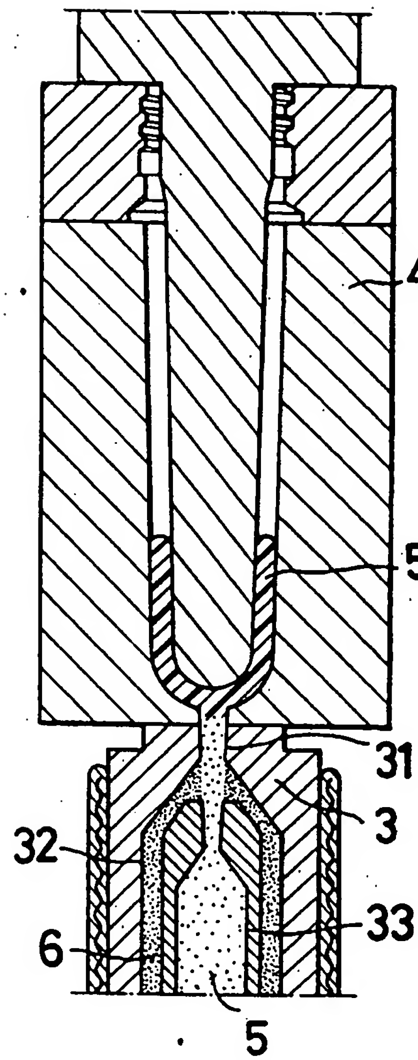


FIG.4A

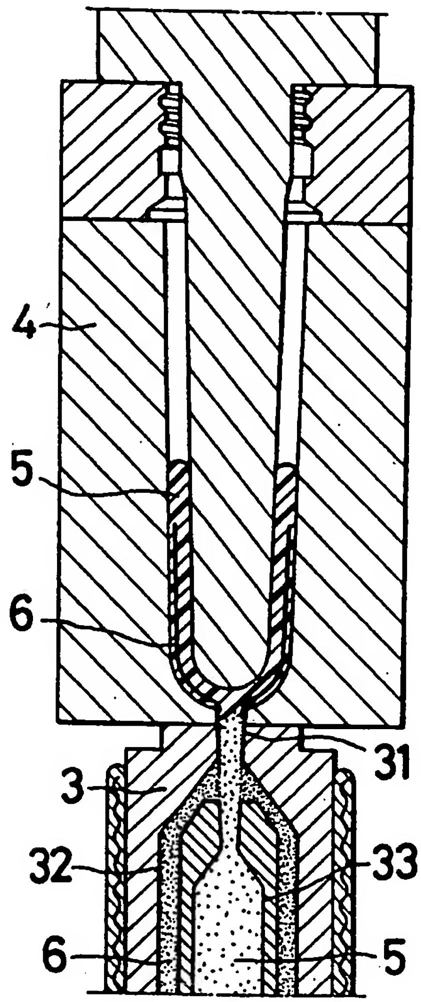


FIG.4B

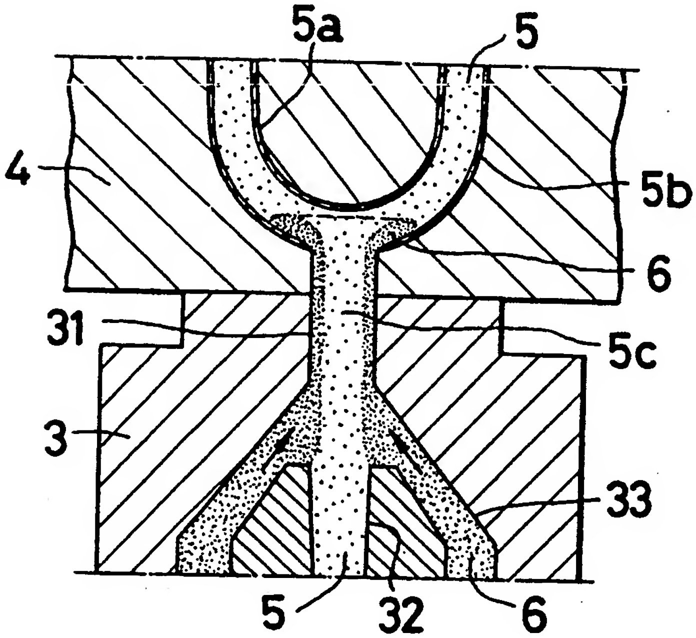
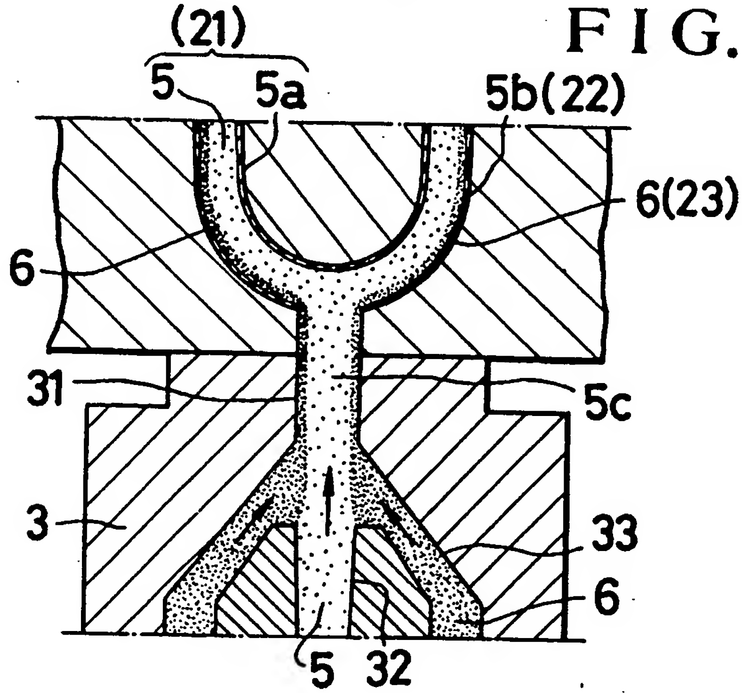


FIG.4C



F I G.5